

[0016] In order to solve the problems considered, the biodegradable wrap film of the present invention is a biodegradable wrap film, comprising, as the main component, a lactic acid resin composition comprising a plasticizer and a poly(DL-lactic acid) in which the proportion of L--isomer and D-isomer is 88:12 to 85:15 or 12:88 to 15:85, comprising, the lactic acid resin composition with a value of storage modulus at 40°C in the range of 100 MPa to 3 GPa as measured at a frequency of 10 Hz and a distortion of 0.1% by the dynamic viscoelasticity testing method from Method A of JIS K-7198 (corresponding to ISO 6721-4; Method A of JIS K-7198 defined on 1 November 1991 is currently replaced by JIS K-7244-4 defined on 20 October 1999), a value of storage modulus at 100°C in the range of 30 MPa to 500 MPa, and a peak value of loss tangent ($\tan \delta$) in the range of 0.1 to 0.8.

[0032] Regarding the DL constitution ratio in poly(DL-lactic acid), for instance, L-isomer:D-isomer = 100:0 to 85:15, or L-isomer:D-isomer = 0:100 to 15:85 is preferred; more preferable from the view point of plasticizer bleed-out is a composition that is less crystalline than at least the L-isomer:D-isomer = 88:12 used in the following Examples 4 to 6, namely, L-isomer:D-isomer = 88:12 to 85:15, or L-isomer:D-isomer = 12:88 to 15:85.

Although a homopolymer is ideally a polymer comprising 100% L-lactic acid or D-lactic acid, as there is the possibility that a different lactic acid is incorporated unavoidably during polymerization, in the present invention, a polymer containing 98% or more L-lactic acid or D-lactic acid is referred to as a homopolymer.

WHAT IS CLAIMED IS:

1. (Amended) A biodegradable wrap film, which is a biodegradable wrap film comprising as a main component a lactic acid resin composition comprising a poly(DL-lactic acid) in which the proportion of L-isomer and D-isomer is 88:12 to 85:15 or 12:88 to 15:85, and a plasticizer, the lactic acid resin composition, wherein

the value of storage modulus at 40°C is in the range of 100 MPa to 3 GPa as measured at a frequency of 10 Hz and a distortion of 0.1% by the dynamic viscoelasticity testing method from Method A of JIS K-7198,

the value of storage modulus at 100°C is in the range of 30 MPa to 500 MPa, and

the peak value of loss tangent ($\tan \delta$) is in the range of 0.1 to 0.8.

2. The biodegradable wrap film as recited in Claim 1, wherein the value of storage modulus at 20°C is in the range of 1 GPa to 4 GPa, as measured at a frequency of 10 Hz and a distortion of 0.1% by the dynamic viscoelasticity testing method from Method A of JIS K-7198, and the value of loss tangent ($\tan \delta$) at 20°C is 0.5 or less.

3. The biodegradable wrap film as recited in Claim 1 or 2, wherein the value of storage modulus at 60°C is in the range of

100 MPa to 800 MPa as measured at a frequency of 10 Hz and a distortion of 0.1% by the dynamic viscoelasticity testing method from Method A of JIS K-7198.

4. The biodegradable wrap film as recited in any of Claims 1 to 3, wherein the lactic acid resin composition comprises a lactic acid resin and a plasticizer in a proportion of 60:1 to 99:1 by mass.

5. The biodegradable wrap film as recited in any of Claims 1 to 4, wherein the difference ($\Delta H_m - \Delta H_c$) is 10 J/g or more between ΔH_m , the heat of melting required to melt the crystals completely when heating the film according to JIS K-7121 at a heating rate of 10°C/minute using a differential scanning calorimeter, and ΔH_c , the heat of crystallization produced concomitantly with crystallization during the heating.

6. The biodegradable wrap film as recited in any of Claims 1 to 5, wherein the formed film is heated at a temperature between the glass transition temperature when heating according to JIS K-7121 at a heating rate of 10°C/minute using a differential scanning calorimeter, and the peak temperature of the heat of crystallization produced concomitantly with crystallization during the heating, and cured for 6 hours or longer.

[0083]
[Table 1]

| | Composition | Storage Modulus | | Peak Value of Loss | Loss Tangent 20°C | $\Delta H_m\text{-}H_{f,c}$ | Stress Ratio | Ability to be Cut | Heat Resistance | Wrapping Suitability | Bleed Acceleration Test |
|-----------------------|---|-----------------|----------|--------------------|-------------------|-----------------------------|--------------|-------------------|-----------------|----------------------|-------------------------|
| | | 20°C MPa | 40°C MPa | | | | | | | | |
| Reference Example 1 | NW4031/TEC=70/30 60°Cx24 hours curing | 2060 | 1200 | 204 | 0.15 | 0.08 | 41 | 1.16 | ○ | ○ | △ X |
| Reference Example 2 | NW4050/TEC=85/15 60°Cx24 hours curing | 2020 | 774 | 125 | 0.2 | 0.13 | 32.3 | 1.18 | ○ | ○ | ○ X |
| Reference Example 3 | NW4050/PX884=90/10 60°Cx24 hours curing | 2400 | 1200 | 167 | 0.19 | 0.07 | 30.1 | 1.08 | ○ | ○ | △ △ |
| Example 1 | NW4060/PX884=90/10 60°Cx24 hours curing | 1990 | 747 | 88 | 0.24 | 0.12 | 21 | 1.09 | ○ | ○ | ○ ○ |
| Example 2 | NW4060/PX884=85/15 60°Cx24 hours curing | 1070 | 433 | 66 | 0.2 | 0.16 | 21 | 1.08 | ○ | ○ | ○ ○ |
| Example 3 | NW4060/PX884=93/7 60°Cx24 hours curing | 3250 | 1260 | 94 | 0.27 | 0.06 | 20 | 1.11 | ○ | ○ | △ ○ |
| Reference Example 4 | NW4031/NW4050/TEC=50/50/40 60°Cx24 hours curing | 1290 | 1930 | 250 | 0.2 | 0.16 | 32 | 1.02 | ○ | ○ | ○ X |
| Reference Example 5 | NW4031/NW4050/NW4060/TEC=45/45/10/30 60°Cx24 hours curing | 3100 | 1970 | 230 | 0.17 | 0.045 | 34 | 1.12 | ○ | ○ | △ △ |
| Comparative Example 1 | NW4031/TEC=70/30 | 1920 | 21 | 110 | 2.6 | 0.15 | 5.1 | 1.02 | × | ○ | ○ X |
| Comparative Example 2 | NW4060/PX884=90/10 | 2450 | 350 | — | 3.1 | 0.052 | 0 | 1.06 | △ | × | ○ ○ |
| Comparative Example 3 | NW4060/PX884=85/15 | 1990 | 11 | 13 | 2.3 | 0.15 | 0 | 1.03 | × | × | ○ ○ |
| Comparative Example 4 | NW4060/PX884=93/7 | 2980 | 1620 | 20 | 1 | 0.03 | 0 | 1.05 | ○ | × | ○ ○ |

(Reference Example 1)

The lactic acid resin NatureWorks 4031D (molecular weight: 200,000), which is a poly(L-lactic acid) with a proportion of L-isomer:D-isomer = 99:1 manufactured by Cargill Dow, and 0.1 phr of aluminum stearate as lubricant were mixed, then melted and extruded at 190°C and 200 rpm using a 40 mmΦ mini co-rotating twin-screw extruder manufactured by Mitsubishi Heavy Industries Co., Ltd., while injecting from the vent opening 30 wt% in mass ratio of triethyl citrate as plasticizer (CITROFLEX 2 (TEC in the table); molecular weight: 270; SP value: 11.46 [fedors method]; manufactured by Morimura Bros., Inc.), and a 10 µm film was formed at a temperature of 200°C by the casting method, which was then cured at 60°C for 24 hours.

(Reference Example 2)

The lactic acid resin NatureWorks 4050 (molecular weight: 200,000), which is a poly(DL-lactic acid) with a proportion of L-isomer:D-isomer = 95:5 manufactured by Cargill Dow, and 0.1 phr of aluminum stearate as lubricant were mixed, then melted and extruded at 190°C and 200 rpm using a 40 mmΦ mini co-rotating twin-screw extruder manufactured by Mitsubishi Heavy Industries Co., Ltd., while injecting from the vent opening 15 wt% in mass ratio of triethyl citrate as plasticizer (CITROFLEX 2 (TEC in the table); molecular weight: 270; SP value: 11.46 [fedors method]), and a 10 µm film was formed at a temperature of 200°C by the casting method, which was then cured at 60°C for 24 hours.

(Reference Example 3)

The lactic acid resin NatureWorks 4050 (molecular weight: 200,000), which is a poly(DL-lactic acid) with a

proportion of L-isomer:D-isomer = 95:5 manufactured by Cargill Dow, and 0.1 phr of aluminum stearate as lubricant were mixed, then melted and extruded at 190°C and 200 rpm using a 40 mmΦ mini co-rotating twin-screw extruder manufactured by Mitsubishi Heavy Industries Co., Ltd., while injecting from the vent opening 10 wt% in mass ratio of adipic acid ester (PX-884; molecular weight: 650; SP value: 11.3 [fedors method]; manufactured by Asahi Denka Co., Ltd.), and a 10 µm film was formed at a temperature of 200°C by the casting method, which was then cured at 60°C for 24 hours.

(Example 1)

The lactic acid resin NatureWorks 4060 (molecular weight: 190,000), which is a poly(DL-lactic acid) with a proportion of L-isomer:D-isomer = 88:12 manufactured by Cargill Dow, and 0.1 phr of aluminum stearate as lubricant were mixed, then melted and extruded at 190°C and 200 rpm using a 40 mmΦ mini co-rotating twin-screw extruder manufactured by Mitsubishi Heavy Industries Co., Ltd., while injecting from the vent opening 10 wt% in mass ratio of adipic acid ester (PX-884; molecular weight: 650; SP value: 11.3 [fedors method]; manufactured by Asahi Denka Co., Ltd.), and a 10 µm film was formed at a temperature of 200°C by the casting method, which was then cured at 60°C for 24 hours.

(Example 2)

The lactic acid resin NatureWorks 4060 (molecular weight: 190,000), which is a poly(DL-lactic acid) with a proportion of L-isomer:D-isomer = 88:12 manufactured by Cargill Dow, and 0.1 phr of aluminum stearate as lubricant were mixed, melted and extruded at 190°C and 200 rpm using a 40 mmΦ mini co-rotating twin-screw extruder manufactured

by Mitsubishi Heavy Industries Co., Ltd., while injecting from the vent opening 15 wt% in mass ratio of adipic acid ester (PX-884; molecular weight: 650; SP value: 11.3 [fedors method]; manufactured by Asahi Denka Co., Ltd.), and a 10 µm film was formed at a temperature of 200°C by the casting method, which was then cured at 60°C for 24 hours.

(Example 3)

The lactic acid resin NatureWorks 4060 (molecular weight: 190,000), which is a poly(DL-lactic acid) with a proportion of L-isomer:D-isomer = 88:12 manufactured by Cargill Dow, and 0.1 phr of aluminum stearate as lubricant were mixed, then melted and extruded at 190°C and 200 rpm using a 40 mmΦ mini co-rotating twin-screw extruder manufactured by Mitsubishi Heavy Industries Co., Ltd., while injecting from the vent opening 7 wt% in mass ratio of adipic acid ester (PX-884; molecular weight: 650; SP value: 11.3 [fedors method]; manufactured by Asahi Denka Co., Ltd.), and a 10 µm film was formed at a temperature of 200°C by the casting method, which was then cured at 60°C for 24 hours.

(Reference Example 4)

The lactic acid resin NatureWorks 4031D (molecular weight: 200,000), which is a poly(L-lactic acid) with a proportion of L-isomer:D-isomer = 99:1 manufactured by Cargill Dow, and the lactic acid resin NatureWorks 4050 (molecular weight: 200,000), which is a poly(DL-lactic acid) with a proportion of L-isomer:D-isomer = 95:5 manufactured by Cargill Dow, were dry-blended at a proportion of 4031D:4050 = 50 wt%:50 wt%, mixed with 0.1 phr of aluminum stearate as lubricant, then melted and extruded at 190°C and 200 rpm using a 40 mmΦ mini co-

rotating twin-screw extruder manufactured by Mitsubishi Heavy Industries Co., Ltd., while injecting from the vent opening 40 wt% in mass ratio of triethyl citrate as plasticizer (CITROFLEX 2; molecular weight: 270; SP value: 11.46 [fedors method]; manufactured by Morimura Bros., Inc.), and a 10 µm film was formed at a temperature of 200°C by the casting method, which was then cured at 60°C for 24 hours.

(Reference Example 5)

The lactic acid resin NatureWorks 4031D (molecular weight: 200,000), which is a poly(L-lactic acid) with a proportion of L-isomer:D-isomer = 99:1 manufactured by Cargill Dow, the lactic acid resin NatureWorks 4050 (molecular weight: 200,000), which is a poly(DL-lactic acid) with a proportion of L--isomer:D-isomer = 95:5 manufactured by Cargill Dow, and the lactic acid resin NatureWorks 4060 (molecular weight: 190,000), which is a poly(DL-lactic acid) with a proportion of L-isomer:D-isomer = 88:12 manufactured by Cargill Dow, were dry-blended at a proportion of 4031D:4050:4060 = 45 wt%:45 wt%:10 wt%, mixed with 0.1 phr of aluminum stearate as lubricant, melted and extruded at 190°C and 200 rpm using a 40 mmΦ mini co-rotating twin-screw extruder manufactured by Mitsubishi Heavy Industries Co., Ltd., while injecting from the vent opening 30 wt% in mass ratio of triethyl citrate as plasticizer (CITROFLEX 2; molecular weight: 270; SP value: 11.46 [fedors method]; manufactured by Morimura Bros., Inc.), and a 10 µm film was formed at a temperature of 200°C by the casting method, which was then cured at 60°C for 24 hours.

(Bleed Acceleration Test)

The following bleed acceleration test was performed

for the films obtained in the above Examples 1 to 3 and Reference Examples 1 to 5. That is to say, a film with 10 cm in the MD direction and 10 cm in the TD direction, was left in an environment of 40°C and 40%RH for 30 days, and the presence or the absence of plasticizer rising onto the film surface was visually observed.

[0084] The result shows that Examples 1, 2 and 3, and Reference Examples 3 and 5 were better compared to Reference Examples 1, 2, and 4. Among these, Examples 1, 2, and 3 were particularly good without any identification of bleeding at all.

Fig. 1

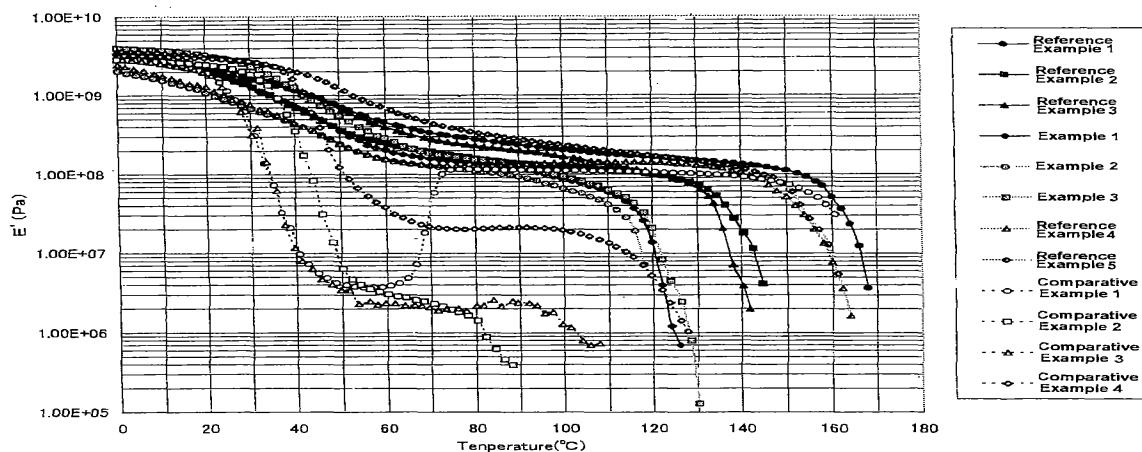


Fig. 2

